ANALYSIS OF PCB CONGENERS ON IONIC LIQUID CAPILLARY COLUMNS

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Introduction

US EPA Method 1668B describes the analysis of PCBs as individual congeners. The method designates the use of an SPB-Octyl column in combination with high resolution mass spectrometry (HRMS) for detection and identification (1). The SPB-Octyl column was chosen by developers for this method due to its ability to resolve the coplanar PCB congeners from interferences. The SPB-Octyl column has limitations, mainly due to phase stability as the phase is susceptible to oxidation and has a maximum operating temperature of 280°C. In this study we evaluate two Ionic Liquid capillary columns: SLB-IL82 and SLB-IL111 to determine if they could provide unique resolution of the toxic coplanar congeners compared to the SPB-Octyl and other capillary columns currently used or the analysis of PCB congeners.

Materials and methods

The elution order of all 209 PCB congeners was determined on the SLB-IL82 and SLB-IL111. For comparison, congener elution order was also determined on the SP-2331. Elution order was determined by injections of a composite mix of all congeners, individual congeners, and specific mix combinations containing known congeners with different degrees of chlorination. Data for the congeners on the SPB-Octyl and SLB-5ms was taken from previous evaluations (2,3).

The analysis conditions were as follows:
Instrument: Agilent 5973 GC-MS system
Columns: (1) SLB-IL82; 30 x 0.25 x 0.20
(2) SLB-IL111; 30 x 0.25 x 0.20
(3) SP-2331: 30 x 0.25 x 0.20
Inj. Temp.: 250 °C
Oven: 50 °C (2 min.), 5 °C/min. to 270 °C
MS Interface: 270 °C
Carrier: helium, 1 mL/min constant flow
MSD: full scan, m/z = 100 to 550
Injection: 1 µL, splitless
Sample: Mix of 209 PCB congeners; 0.5 ug/ml – 1.5 ug/ml in isooctane

Results and discussion:

Resolution of toxic coplanar congeners. The toxic coplanar congeners, as designated by the World Health Organization (WHO), and specified in Method 1668B, are #77, #81, #105, #114, #118, #123, #126, #156, #157, #167, #169, and #189. These congeners all contain 4 or more chlorines, and contain either 1 or no chlorines in the ortho position. They are referred to as "coplanar" PCBS due to the ability to exist spatially as either flat "within-the-plane" or partially twisted "out-of-the-plane" molecules. The impact of this "coplanar" ability allows these congeners to act like dioxins within the body, giving them toxic characteristics.
For accurate identification and quantitation of the coplanar congeners, resolution must be unique, either chromatographically or by mass. Coplanar congeners that coelute with another congener that has the same number of chlorines cannot be resolved by mass. As a result, the coeluting congener will prevent the accurate identification and quantitation of the coplanar.
The total number of coelutions for each polar column was compared with data previously generated on the SPB-Octyl and SLB-5ms:

	SPB-Octyl (3)	SLB-5ms (4)	SP-2331	SLB-IL82	SLB-IL111
# coelutions (total)	37	21	62	68	56
# of coplanars that coelute with other congeners	4	1	6	4	3

In the case of the SPB-Octyl, two hexachlorinated coplanar congeners, #156 and #157, coelute with each other. However, according to Method 1668B, this is acceptable since both are toxic coplanars and have the same toxic equivalency factor (TEF), and thus can be reported together. On the SLB-5ms, coplanar congener #170 coelutes with non-coplanar congener #190. Both congeners are heptachlorinated and thus #170 cannot be accurately determined.

A more detailed summary of the elution of the coplanar congeners on the SP-2331, SLB-IL82, and SLB-IL111 columns is presented in the table below:

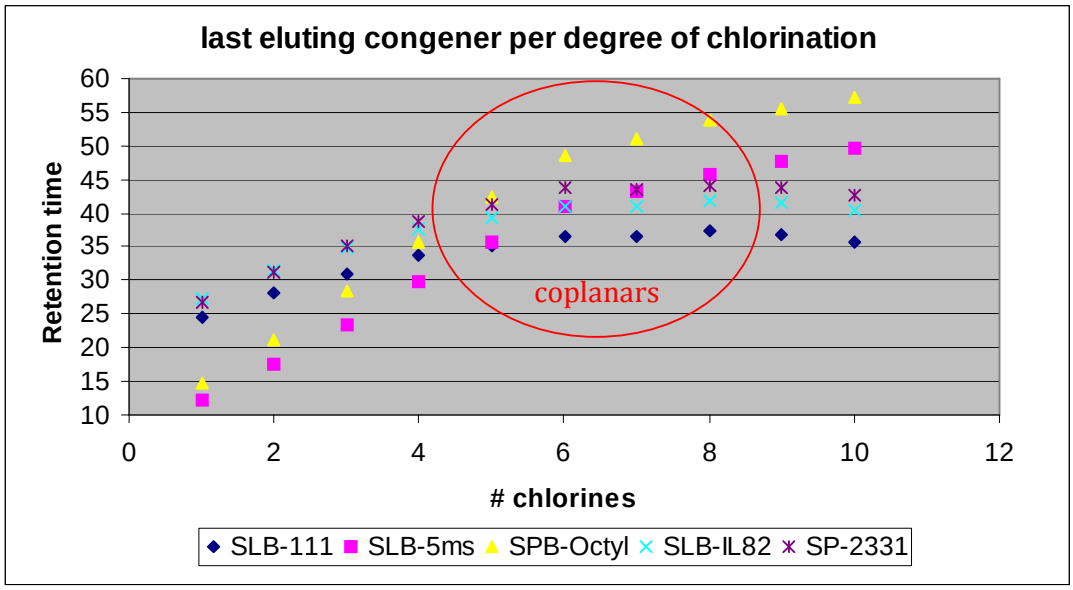
	SP-2331	SLB-IL82	SLB-IL111
#77 (3,3',4,4-TeCB)	No coelutions	coelutes w/#129	No coelutions
#81 (3,4,4',5-TeCB)	coelutes w/#200	No coelutions	coelutes w/#162
#105 (2,3,3,4,4'-PeCB)	No coelutions	coelutes w/#191	coelutes w/#196
#114 (2,3,4,4',5-PeCB)	No coelutions	coelutes w/#159	colelutes w/#164
#118 (2,3',4,4',5-PeCB)	coelutes w/#178	No coelutions	coelutes w/#106 & #200
#123 (2',3,4,4',5-PeCB)	coelutes w/#142&110	coelutes w/#178	coelutes w/#204
#126 (3,3',4,4',5-PeCB)	coelutes w/#156	No coelutions	coelutes w/#156
#156 (2,3,3',4,4',5-HxCB)	coelutes w/#126	No coelutions	coelutes w/#126
#157 (2,3,3',4,4',5'-HxCB)	No coelutions	No coelutions	No coelutions
#167 (2,3',4,4',5,5'-HxCB)	No coelutions	No coelutions	No coelutions
#169 (3,3',4,4',5,5'-HxCB)	coelutes w/#206	No coelutions	No coelutions
#189 (2,3,3',4,4',5,5-HxCB)	No coelutions	No coelutions	No coelutions

#106, #110, #126: PeCB
#129, #142, #156, #159, #162, #164: HxCB
#178, #191: HpCB
#196, #200, #204, #206: OcCB

- On the SP-2331, the coelution of #123 and #110 is critical, as both are pentachlorinated congeners
- On the SLB-IL111, the coelution of #118 and #106 is critical, as both are pentachlorinated congeners
- On the SLB-IL82, no coplanars coeluted with other congeners of the same degree of chlorination. This is also the case for the SPB-Octyl.

Retention characteristics. Retention of the coplanars was longer compared to other congeners with the same degree of chlorination. This is consistent with behavior observed on the SPB-Octyl and the SLB-5ms. On nonpolar columns such as the SPB-Octyl and SLB-5ms, overall retention increases with the degree of chlorination. By comparison, polar columns are less retentive for the relatively nonpolar PCB congeners. Figure 1 illustrates a comparison of the retention times of the last eluting congener for each degree of chlorination for several different column chemistries. The congeners eluted during the oven ramps used for all five columns shown in Figure 1. Retention is seen to increase with degree of chlorination on both the SPB-Octyl and SLB-5ms. However on the SP-2331 and ionic liquid columns, retention levels off slightly and then shows a slight decrease from hexa – deca chlorinated. This indicates the predominance of retention mechanisms other than dispersive at higher temperatures.

Figure 1. Retention times of last eluting congener for each degree of chlorination



Conclusions

- SLB-IL82 and SLB-IL111 are compatible with PCB congeners in that they exhibit acceptable peak shape and response.
- As expected, retention of PCB congeners is not as strong as that exhibited by nonpolar phases such as SPB-Octyl and SLB-5ms. Retention was similar to the SP-2331.
- Within each degree of chlorination, retention of the coplanar congeners tended to be longer than noncoplanars. This is consistent with behavior exhibited by the SPB-Octyl, SLB-5ms, and SP-2331.
- SLB-IL82 shows potential for resolution of the 12 toxic coplanar PCB congeners. All coelutions exhibited by coplanars are with congeners of different degrees of chlorination. If a high resolution mass spectrometer is used for detection, this may be acceptable for some applications.
- The SLB-IL111 does not resolve all coplanars from congeners with the same degree of chlorination. Congener #118, a coplanar, coelutes with #106. Both are pentachlorinated congeners.
- Both ionic liquid columns exhibited more total coelutions than the SPB-Octyl. This is partially due to the shorter retention of the congeners on these columns.

References:

1. US EPA Method 1668B, November 2008.
2. Supelco Application Note 158, Analysis of 209 PCB Congeners on the SPB-Octyl and MDN-5S Columns.
3. Supelco Application Request #257, Analysis of 209 PCB Congeners on the SLB-5ms, December 2008.